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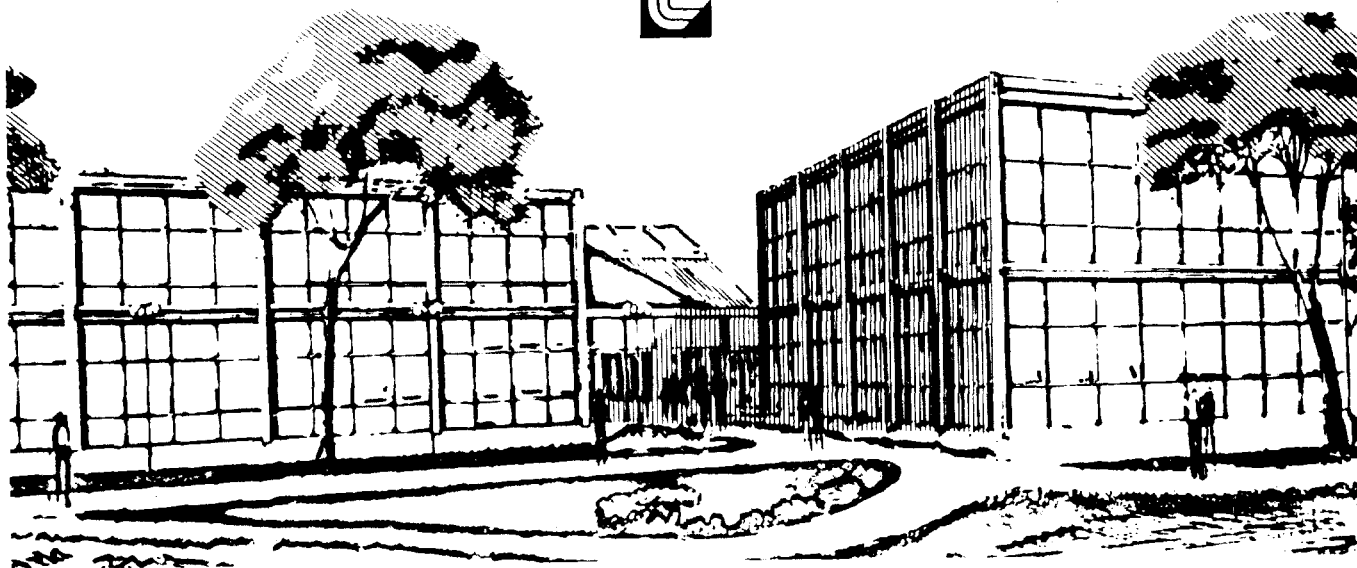
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AT THE SALTON SEA GEOTHERMAL FIELD

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FIELD TESTS OF ORGANIC ADDITIVES FOR THE CONTROL OF SCALE  
AT THE SALTON SEA GEOTHERMAL FIELD\*

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ABSTRACT

A variety of organic compounds have been evaluated for potential use in the reduction of silica scale formed from hypersaline brine. A brine treatment test system for operation from Magmamax No. 1 and Woolsey No. 1 wells was assembled and used for the testing of the additives. Injection of prospective compounds at  $\sim 200^\circ\text{C}$  and measurement of silica precipitation rates in the effluent brine revealed the following classes of substances to be effective inhibitors: hydroxyethylcelluloses, polyoxyethylenes, other compounds with high ethylene oxide content, polyethylene imines, and ethoxylated quaternary ammonium compounds. One compound, Ethoquad 18/25 [Armak methylpolyoxyethylene(15) octadecylammonium chloride], was found to retard the deposition and change the morphology of the silica-rich scales in the 90-125°C temperature range.

INTRODUCTION

Utilization of the hypersaline brines of the Salton Sea Geothermal Field for power generation, mineral recovery, and direct use is now in the early stages of development. However, the successful commercialization of these ventures will depend in part on avoiding or controlling the severe scaling that occurs in plant structures when the brines are cooled. These scales range in composition from primarily heavy-metal sulfides at well-head temperatures ( $\sim 200^\circ\text{C}$ ) to nearly "pure" silica at the temperatures of effluent brine ( $\sim 100^\circ\text{C}$ ). The highly siliceous scales represent the greatest problem because they can accumulate at the highest rates ( $\sim 0.001$  in./h), techniques for their removal are costly, and no methods for their abatement by chemical treatment of the brine have won wide acceptance. Brine acidification is the only chemical method that has been clearly demonstrated(1,2) to decrease the rate of formation of geothermal siliceous scales, but this treatment technique requires the use of more-highly corrosion-resistant, expensive plant materials and is itself costly.

Since late 1977, in a program aimed at finding an effective alternative to the technique of brine acidification for geothermal scale control, the Lawrence Livermore Laboratory has been screening and evaluating a number of commercial organic and inorganic chemicals as inhibitors of silica precipitation and scaling. The first bench scale tests(3) revealed that several compounds containing the oxyethylene moiety,  $-\text{CH}_2-\text{CH}_2-\text{O}-$  (i.e., polyethylene oxide), were effective in stabilizing colloidal silica in geothermal brine.

To continue this investigation, we have constructed a small-scale brine treatment test facility, and evaluated under pilot plant conditions a selection of commercial, proprietary chemical mixtures that were submitted for test as scale inhibitors(4). Although many such mixtures are beneficial in the abatement of scale in other applications (where, for example, the scale is crystalline  $\text{CaCO}_3$  or  $\text{CaSO}_4$ ; or even silica in conventional boilers), none of the proprietary products performed sufficiently well in our scaling-rate measurements to merit recommendation. It is obvious that the high-temperature, very-high-salinity, high-silica brines of the Salton-Sea Geothermal Field are rather unusual in the science of aqueous colloid chemistry, and that the traditional approaches to scale control are of marginal effectiveness in these systems.

This paper describes the results of further tests of a variety of commercially-available, generic chemical compounds that we have selected as candidates for the inhibition of silica scale. In this work we hoped to gain further knowledge concerning the specific interactions between colloidal silica and the active compounds(3), and perhaps find a truly effective inhibitor that could be used in a large-scale facility. Our approach in screening compounds for subsequent scaling tests has been to inject the additive into the brine at high temperature, where it remains as the brine is flashed; withdraw a sample; and then measure the effect of the additive on the rate of precipitation of silica from brine held at  $90^\circ\text{C}$ . We have not completely discounted the possibility that an agent may be found that reduces the scale without stabilizing colloidal silica, but we have chosen to screen additives via the precipitation tests as the most rapid and most probable route to an effective antiscalant.

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## EXPERIMENTAL METHODS

The system assembled for testing the scale control additives is shown schematically in Figure 1. In this apparatus two-phase fluid from the geothermal well is first passed through a centrifugal-type separator. The steam is discarded and single-phase brine is obtained at nearly well-head temperature and pressure. The brine is then divided into two nominally identical channels for testing of the additives. The brine in each channel is flashed to 125°C in flash vessels and then passed to an atmospheric receiver. The "delay stage" provides brine at atmospheric pressure, a temperature of 90-100°C, and aged ~10 min. with respect to the 125°C flash.

Brine flow is maintained in each channel at 7.0 gal/min (~1 lb/sec) by monitoring the pressure drop (~15 in. H<sub>2</sub>O) across an orifice plate that is cleaned periodically. Additive solution (at about 0.5-1.0% strength) is metered into the brine using high-pressure pumps equipped with pulsation dampers, and this flow is monitored by means of turbine flow meters and maintained in the range of 0.02-0.04 gal/min. The additive solution is introduced into the flowing brine through a concentric 1/4-in. tube ~8 ft. upstream from the first test specimen. The accuracy of maintaining a desired concentration of additive was determined in a tracer study using cesium ion and found to be ±10%.

The scaling tendency of the brine is measured at various points in the system by the use of specimen pipe spools, flat coupons, small-diameter tubing, and perforated disks. As an indirect measure of scaling tendency, corrosion rates of materials exposed to the brine are estimated using Petrolite Instruments linear polarization resistance (LPR) equipment.

To measure the effect of the additives on the rate of precipitation of silica, brine samples are collected for study from the 125°C sampling ports. During sampling, the brine flashes to 105°C. It is then placed in air-tight, Viton-gasketed, 130-ml, screw-cap glass bottles and incubated at 90°C. At appropriate intervals after sampling, the bottles are opened and the contents filtered through fine-porosity glass crucibles. The silica remaining in the filtrate is measured by atomic absorption spectrophotometry using the method of standard additions. Measurement of the silica in this manner has been shown to yield values for the total concentration of silica (monomeric, polymeric, and particulates <1 µm in size) not retained by the filter. The initial concentration of silica in the brine sampled at the effluent port was determined in samples immediately acidified with hydrochloric acid. The collected solids are dried in air at 105°C and weighed as a measure of the suspended solids concentration of the brine.

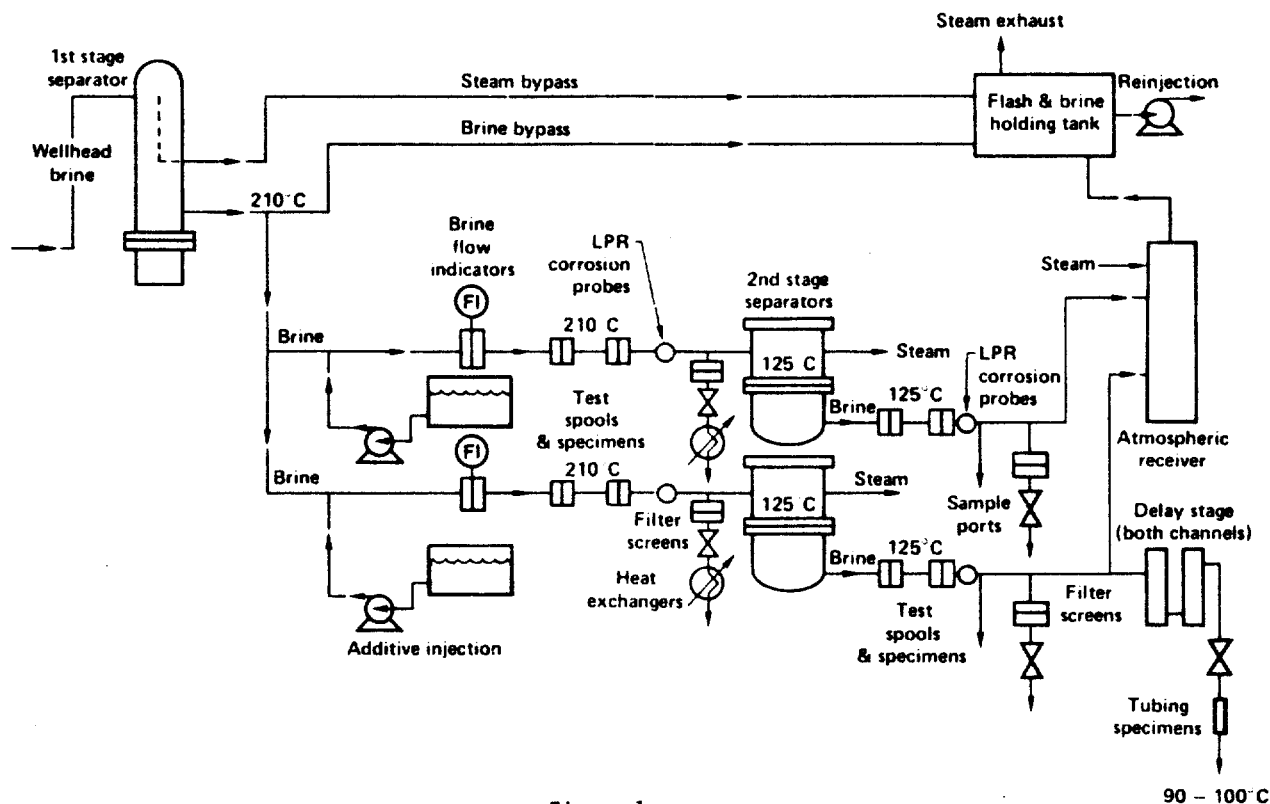


Figure 1  
Schematic Diagram of LLL Brine Treatment Test System

Table 1. Types and examples of organic compounds that inhibit the precipitation of silica from hypersaline geothermal brine. (20 ppm additive; Magmamax No. 1 brine).

Trade Name	Manufacturer	Chemical Name <sup>a</sup>	Brine characteristics after 1 hour incubation at 90°C	
			Concentration of suspended solids, mg/kg	Silica retained, %
Untreated Brine - Control			257 ± 38	47 ± 4
Hydroxyethylcelluloses (HEC)				
Natrosol 250LR	Hercules	HEC, M.W.=85,000	90	88
Polymer JR-125	Union Carbide	Amine-substituted HEC	125	68
Polyoxyethylene Polymers:				
Carbowax 14,000	Union Carbide	Polyoxyethylene, M.W.=14,000	102	89
Ethoxylated Amines:				
Ethomeen 18/25	Armak	Polyoxyethylene(15) octadecyl- amine	67	95
Ethomeen 18/60	Armak	Polyoxyethylene(50) octadecyl- amine	59	92
Ethomeen C/25	Armak	Polyoxyethylene(15) cocoamine	153	78
Quaternary Ammonium Compounds:				
Ethoquad 18/25	Armak	Methylpolyoxyethylene(15) octadecylammonium chloride	54	94
Hyamine 1622	Rohm & Haas	Di-isobutylphenoxyethoxyethyl- dimethylbenzylammonium chloride	81	85
Q-C-50	Tomah	Methylpolyoxyethylene(50) cocoammonium chloride	97	85
Other Ethoxylated Compounds:				
Pluronic F38	BASF-Wyandotte	Polyoxyethylene/polyoxypropylene block copolymer, M.W.=5000	133	74
Conco NI-125	Continental	Polyoxyethylene(200) nonyl phenol	110	73
Lipal 200C	PVO Int'l	Polyoxyethylene(200) ricinoleic acid triglyceride	111	73
Jeffox FF-200	Jefferson	Polyoxyethylene/polyoxypropylene random copolymer, M.W.=10,000	193	62
Miscellaneous Compounds:				
Corcat P-200	Cordova	Polyethylene imine, M.W.=20,000	105	88
XD-8779.00	Dow Chemical	Polyethyloxazoline, M.W.=60,000	244	60

<sup>a</sup>Number in parentheses denotes the number of molecules of ethylene oxide per molecule of additive.

#### BRINE CHARACTERISTICS

The precipitation and scaling tests were conducted with Magmamax No. 1 and Woolsey No. 1 brine having the following major characteristics (effluent): 3.7-4.5 Mol/l chloride, pH 5.7-6.0, and 470-520 mg/kg SiO<sub>2</sub>.

#### RESULTS AND DISCUSSION OF PRECIPITATION TESTS

Over 75 substances representing a number of different classes of organic compounds have been examined thus far for their effect on silica in hypersaline geothermal brine (4,5). Those found to be most effective as precipitation inhibitors are listed in Table 1. As was conjectured previously (3), it is now clear that the oxyethylene moiety is indeed the principal source of activity in many of these substances. Cellulose derivatives without ethylene oxide have no activity. Essentially pure ethylene oxide polymers, in the form of the Carbowaxes (Union Carbide), are very potent inhibitors, and their peak activity occurs

at a molecular weight of ~14,000 (5,1).

The activity of the nitrogen-containing compounds illustrates that the oxyethylene moiety is not unique in interacting with the silica. The polyethylene imines appear especially promising, as does another compound, PAE-HCl (Dynapol), which is a poly(aminoethylene, HCl salt). This substance is not listed in Table 1 because it was examined under different brine conditions, but recent tests showed that it is a strong inhibitor. In contrast to the cationic substances and non-ionic compounds containing ethylene oxide, anionic compounds such as the phosphonates, sulfonates, phosphate esters, and acrylic-type compounds have shown little activity toward silica under these conditions.

#### MECHANISM OF INHIBITION

It is probable that the inhibition of silica precipitation that we have demonstrated is an example of the steric stabilization of colloidal

systems(6). This entails the adsorption of the stabilizing molecules on the surfaces of the colloidal particles to retard or prevent their aggregation. In the case of the polyoxyethylenes, hydrogen bonding(7) between the silanol groups and the oxygens or terminal hydroxyls of the polymer may be involved. It appears that the ideal molecule for application here would be one that anchors itself tightly to the surface of the colloidal particles, presents a hydrophilic moiety to the aqueous medium, and is a certain minimum molecular size to produce steric repulsion. The particles on which it is adsorbed would thus remain solubilized and dispersed.

Weakly adsorbed dispersants are vulnerable to "displacement flocculation," which is the dislodgement of adsorbed molecules by Brownian motion collisions of the particles, leading to aggregation(6). Flocculation is enhanced by high rates of fluid shear(8), such as exist in geothermal systems. Thus, *in situ* scaling tests are considerably more severe than colloidal stability measurements of the type we have used to screen potentially useful additives. However, the precipitation tests are valid for the relative ranking of compounds, and injection of the additives in the manner described reveals their resistance to the rigorous, high-temperature conditions of the input brine.

#### SCALING TESTS

Several of the most promising precipitation inhibitors have been tested to determine their effects on the scaling tendency of the flowing brine. Exposure times have not yet been sufficiently long to measure influences on scaling rates at 200°C, which are <0.1 mil/h, but good measurements of rates at 125°C (3-day tests) and 90°C (24-h exposures) have been obtained. To distinguish purely scaling effects from those due to corrosion, scaling rates were measured using three materials: mild steel, Teflon, and Hastelloy.

All of the precipitation inhibitors tested as antiscalants had the effect of diminishing the scale formed at temperatures <100°C -- the type that is formed in atmospheric receivers and downstream equipment. These include Natrosol 250 LR(4), Ethomeen C/25 and 18/60, and Carbowax 14,000. Carbowax produced a significant 70% reduction of the scaling rate at 90°C (5,1); however, the latter three compounds increased the scaling rate at 125°C, probably through the formation of a pseudo-scale(9), in which the additive, because of limited solubility at the elevated temperature, is itself incorporated into the deposit. The best scale inhibitor tested thus far is Ethoquad 18/25, which, being an ionic salt, does not possess the high temperature limitations of the nonionic compounds. It was found to reduce the scale at 90°C by 70% and the scale at 125°C by 40%, and it rendered the scale that was formed at these temperatures easier to remove. Further work will focus on optimizing inhibitor response within the most promising classes of compounds, and the possible use of combinations of organic inhibitors with pH adjustment of the brine.

#### ACKNOWLEDGMENTS

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Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the Department of Energy to the exclusion of others that may be suitable.

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